(19) Europäisches Patentamt
Eur pean Patent Office
Offic eur péen des brevets

(11) Publication number: 0 174 875 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 85306567.0

(22) Date of filing: 16.09.85

(51) Int. Cl.[4]: G 21 K 4/00
C 09 K 11/08

(30) Priority: 14.09.84 JP 195146/84
14.09.84 JP 195147/84
14.09.84 JP 195148/84
14.09.84 JP 195149/84
18.09.84 JP 196366/84
18.09.84 JP 196367/84

(43) Date of publication of application: 19.03.86 Bulletin 86/12

(84) Designated Contracting States: DE NL

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(54) Method for converting radiographic image and radiation energy storage panel having stimulable phosphor-containing layer.

(57) Disclosed are a method for converting radiographic image which comprises the steps of:

(a)storing radiation energy-corresponding to a radiographic image in a stimulable phosphor of a panel comprising a stimulable phosphor-containing layer.

(b)scanning the layer with a stimulating ray to release the stored energy as a fluorescence, and

(c)detecting the fluorescence to form an image, wherein the stimulable phosphor is represented by the following formula:

$$(M_{1-x}\cdot M^{I}_{x})X\cdot aM^{II}X'_2\cdot bM^{III}X''_3\cdot cA:dB$$

wherein M represents either Cs or Rb; M^{I} represents at least one of alkaline metals selected from the group consisting of Li, Na, K, Rb and Cs; M^{II} represents at least one divalent metal selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni; M^{III} represents at least one metal selected from the group consisting of Se, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Cd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In; A represents at least one metal oxide selected from the group consisting of BeO, MgO, CaO, SrO, BaO, ZnO, Al_2O_3, Y_2O_3, La_2O_3, In_2O_3, SiO_2, TiO_2, GeO_2, SnO_2, Nb_2O_5, Ta_2O_5 and ThO_2; B represents at least one metal selected from the group consisting of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu, Mg, Pb, Bi, Mn, and In; X, X' and X" each may by the same or different and represent a halogen atom selected from F, C, Br and I; x, a, b, c and d are numerals in the range of $0 \leq x \leq 1$, $0 \leq a \leq 1$, $0 \leq b \leq 0.5$, $0 < c < 0.5$ and $0 < d \leq 0.2$, respectively, and a radiation energy storage panel having a stimulable phosphor-containing layer characterized in that the stimulable phosphor comprises the compound having the above formula.

The radiation energy storage panel using the present stimulable phosphor is superior in water vapor resistance to the panel using the prior art stimulable phosphor and can greatly improve lowering in stimulable emission luminance with lapse of time.

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Method for converting radiographic image and radiation energy storage panel having stimulable phosphor-containing layer

BACKGROUND OF THE INVENTION

This invention relates to a method for converting radiographic image and a radiation energy storage panel having a stimulable phosphor-containing layer, more particularly, it is concerned with a method for converting radiographic image utilizing a stimulable phosphor and a radiation energy storage panel utilizing an alkali halide phosphor activated with thallium and the like.

Hitherto, there has been employed the so-called radiography using a silver salt for a radiation image, but there has now been desired a method for making a radiation image without using any silver salt.

Instead of the aforesaid radiography, there has been reviewed a method wherein radiation transmitted through the subject is absorbed in a phosphor, the phosphor is excited with a center energy to emit a radiation energy having accumulated in said phosphor as fluorescence and the fluorescence is detected to form an image. Illustra-

tively, there has been proposed a method wherein a thermostimulable phosphor is used as a phosphor and a radiation image is converted by using a thermal energy as an exciting energy [see British Patent No. 1,462,769 and Japanese Provisional Patent Publication No. 29889/1976]. This conversion method is to employ a panel having a thermostimulable phosphor layer formed over a support, absorb a radiation transmitted through the subject into the thermostimulable phosphor layer of said panel so as to accumulate radiation energy upon strength and weakness of radiation, heat the thermostimulable phosphor layer to take out the accumulated radiation energy as a photosignal and then form an image upon strength and weakness of the luminescence. However, this method required heating for converting radiation energy to a photosignal and thus needed absolutely that the panel has a heat resistance without any modification or deformation by heat. Thus, there was a great restriction to a thermostimulable phosphor layer forming a panel, a raw material for a support and the like. There is thus seen a great difficulty in practical application with regard to this method for converting radiographic image using a thermostimulable phosphor as a phosphor and a thermal energy as an exciting energy. On the other hand, there has been also known another method for converting radiographic image wherein one uses a panel having a stimulable phosphor-containing layer placed over a support and as an exciting energy either or both of visible light and infrared light (see U.S. Patent No. 3,895,527). This latter method may be said to be a more preferable method for converting radiographic image, in view of no heating required for converting the accumulated radiation energy to a photosignal as done in the former method and no need for heat resistance of a panel.

Among the phosphors employed in the aforesaid method for converting radiographic image, there have been known as a

thermostimulable phosphor such phosphors as LiF:Mg, $BaSO_4$:Mn, CaF_2:Dy and the like. Moreover, there have been known such phosphors as KCl:Tl or BaFX:Eu^{2+} type (X: Cl, Br, I) phosphor as disclosed in Japanese Provisional Patent Publication No. 75200/1984 as a stimulable phosphor using as an exciting energy a visible light or an infrared light.

Now, where the said method for converting radiographic image is to be applied to X-ray image conversion for medical diagnosis, the method is desirably of a high sensitivity as far as possible in order to reduce an exposed dose for patients, so that it is desired that the stimulable phosphor used for the method may show a high emmision luminance by stimulation as far as possible.

In the above-mentioned method, a reading speed for radiation image should be made higher for enhanced operation efficiency as a system and, therefore, a stimulable phosphor may desirably have a rapid response speed of stimulable emission to an exciting light.

In the above-mentioned method, a radiation energy storage panel is repeatedly used after elimination of the residual image formed by previous use; however, it is desirable that an elimination time for residual image should be short in said radiation energy storage panel and also that the stimulable phosphor used in the method should have a rapid elimination time for residual image.

However, the above stimulable phosphors are not completely satisfactory in all respects to stimulable emission luminance, response speed to stimulable emission and elimination speed for residual image and there has been desired an improvement in them.

Additionally, a reading apparatus for taking radiation

image in the above methods should be desirably miniaturized, of a low cost and simplified and, thus, it is essential to use as an exciting light source a semi-conductor laser rather than a gas laser, e.g., an Ar^+ laser, an He-Ne laser and the like. Accordingly, it is desirable that the stimulable phosphor employed in this method should desirably have a stimulable exciting spectrum adaptable to an oscillating wave length (not less than 750 nm) of a semi-conductor laser.

However, the above stimulable phosphor does hardly exert a stimulable emmision to an oscillating wave length of a semi-conductor laser and thus there has been desired a longer wave length of a stimulable exciting spectrum.

As the alkali halide phosphor, there have been also known CsI:Na, CsI:Tl, CsBr:Tl, RbBr:Eu, RbCl:Eu, KCl:Tl, LiF:Mg and the like. Among them, CsI:Na or CsI:Tl has been applied to I.I. tube for X-ray, while CsBr:Tl has been tried for application to a similar use. Also, it is known that RbBr:Eu, RbCl:Eu or LiF:Mg be a thermostimulable phosphor and that KCl:Tl may show a stimulable phenomenon.

It was seen that a stimulable phosphor may be utilized as an accumulated radiation energy storage panel by absorbing radiation transmitted through the subject, emitting as fluorescence the radiation energy having accumulated in the phosphor by irradiation with either or both of visible light with a longer wave length and infrared light and detecting said fluorescence to form a radiation image of the subject. But, when applied as such a radiation energy storage panel, the subjects may be frequently human beings, therefore, there is needed a less exposed dose to the subject as far as possible and there is desired as the phosphor therefor a phosphor having a higher stimulable emission efficiency. Further,

a scanning time per one image element is practically about 10 μsec from the relationship with a reading time and a resolving power and a readable area in a radiation energy storage panel and then there is desired a phosphor having a shorter shelf life of stimulable emission. And further, the afterglow from stimulable emission on reading, if any, may cause deterioration of a SN ratio and then there is desired a phosphor showing no such an afterglow phenomenon.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for converting radiographic image comprising absorbing a radiation transmitted through the subject in a stimulable phosphor, exciting the stimulable phosphor with an electromagnetic wave in the region of visible light and/or infrared light or ray to emit the accumulated radiation energy in the stimulable phosphor and detecting such a fluorescence, wherein there is employed a stimulable phosphor showing emission of a higher luminance with a higher sensitivity.

It is another object of this invention to provide a method for converting radiographic image which employs a stimulable phosphor having a rapid response speed of stimulable emission to an exciting light so that reading is possible at a high speed.

Another object of this invention is to provide a method for converting radiographic image with a short elimination time for residual image which employs a stimulable phosphor having a rapid elimination speed for residual image upon repeated uses.

A further object of this invention is to provide a method for converting radiographic image wherein there is used a

stimulable phosphor having a broadened stimulable excited spectrum up to a near infrared region and a semi-conductor laser may be employable as an exciting light.

A still another object of this invention is to provide a method for converting radiographic image which employs an alkali halide type stimulable phosphor having a superior water-vapor resistance without any problem on reduction in an emission luminance by stimulation with lapse of time.

Further, an object of this invention is to provide a radiation energy storage panel which can satisfy the aforesaid objects.

The present inventors have made various studies on a stimulable phosphor which may exert a stimulable emission with a higher luminance for meeting the aforesaid objects and also present no problem on reduced emission luminance by stimulation with time, and, as a result, it has been found that the present objects can be accomplished by a method of converting a radiographic image wherein it comprises the steps of:

(a) storing radiation energy-corresponding to a radiographic image in a stimulable phosphor of a panel comprising a stimulable phosphor-containing layer,

(b) scanning said layer with a stimulating ray to release said stored energy as a fluorescence, and

(c) detecting said fluorescence to form an image, wherein said stimulable phosphor is represented by the following formula [I]:

$$(M_{1-x}\cdot M^{I}_{x})X\cdot aM^{II}X'_{2}\cdot bM^{III}X''_{3}\cdot cA:dB \qquad [I]$$

wherein M represents either Cs or Rb; M^I represents at least one of alkaline metals selected from the group consisting of Li, Na, K, Rb and Cs; M^{II} repre-

sents at least one divalent metal selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni; M^{III} represents at least one metal selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In; A represents at least one metal oxide selected from the group consisting of BeO, MgO, CaO, SrO, BaO, ZnO, Al_2O_3, Y_2O_3, La_2O_3, In_2O_3, SiO_2, TiO_2, ZnO_2, GeO_2, SnO_2, Nb_2O_5, Ta_2O_5 and ThO_2; B represents at least one metal selected from the group consisting of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu, Mg, Pb, Bi, Mn and In; X, X' and X" each may by the same or different and represent a halogen atom selected from F, Cl, Br and I; x, a, b, c and d are numerals in the range of $0 \leq x \leq 1$, $0 \leq a \leq 1$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.5$ and $0 < d \leq 0.2$, respectively.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows response characteristics of a stimulable phosphor;

Fig. 2 shows residual image elimination characteristics of a stimulable phosphor;

Fig. 3 is a flow sheet briefing an embodiment of the present method;

Fig. 4 shows a stimulable emission spectrum of the present stimulable phosphor sample;

Fig. 5 shows an excited spectrum of the above phosphor sample;

Figs. 6 and 7 show stimulable emission spectra of one phosphor sample of this invention;

Figs. 8 and 9 show stimulable excited spectra of the above phosphor sample; and

Fig. 10 shows a diagram showing the results from a forced humidity test.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The alkali halide stimulable phosphor having the composition according to this invention, when excited with an electromagnetic wave in the region of from visible to up to infrared, can exert a higher luminance of stimulable emission than the prior alkali halide type stimulable phoshor does and, moreover, there can be provided a method for converting radiographic image presenting no problem on lowered stimulable emission luminance with lapse of time.

The method for converting radiographic image of this invention may be practiced by the use of a radiation energy storage panel containing a stimulable phosphor having the above formula [I].

A radiation energy storage panel comprises basically a support or a base and at least one stimulable phosphor-containing layer provided over either side or both sides thereof. Generally, there is provided over the surface of the opposed side on a support to said stimulable phosphor-containing layer a protective layer for chemically or physically protecting said stimulable phosphor-containing layer. More specifically, the method for converting radiographic image according to this invention may be embodied by the use of a radiation energy storage panel comprising substantially a support and at least one stimulable phosphor-containing layer placed over the said support, characterized in that at least one layer of said stimulable phosphor layers

contains a stimulable phosphor represented by the above formula [I].

The stimulable phosphor of the above formula [I], after absorbing such radiation as X-ray and the like, may exhibit a stimulable emission when irradiated with a light in the visible or infrared region, preferably a light in a wave length region of 500 - 900 nm (namely, an exciting light). Accordingly, a radiation transmitted the subject or emitted from the subject may be absorbed with the stimulable phosphor contained in the stimulable phosphor-containing layer of a radiation energy storage panel, proportionally to a radiation amount or dose, and the subject or radiation image thereof may be formed on said radiation energy storage panel as a latent image having accumulated therein a radiation energy. This latent image may show a stimulable emission proportional to the accumulated radiation energy by excitation with an exciting light having a wave length region of not less than 500 nm and then the latent image having accumulated therein a radiation energy may be made to a visible image by a photoelectric reading of said stimulable emission.

This invention will be more fully illustrated below by referring to the accompanied drawings.

Fig. 1 shows the response characteristics to an exciting light by a stimulable phosphor represented by the above formula [I] which may be applied to the present method for converting radiographic image, as compared with the stimulable phosphor in the prior art method.

In Fig. 1, (a) indicates response characteristics to a exciting light by a stimulable phosphor employable for the present method for converting radiographic image, while (b) and (c) show, respectively, response character-

istics of the prior art stimulable phosphor, BaFBr:Eu and BaFCl:Eu, a dotted line showing the state of an exciting light having a recutangularly variable strength.

As apparent form Fig. 1, a stimulable phosphor, which may be employed for the present method for converting radiographic image, has remarkably superior response characteristics to an exciting light, which may lead to a higher reading speed for radiation image, as compared with the prior art method.

Fig. 2 shows residual image elimination characteristics by a stimulable phosphor represented by the above formula [I] which may be employed for the present method for converting radiographic image, as compared with the stimulable phosphor in the prior art method.

In Fig. 2, (d) shows decay characteristics of accumulated energy as seen when a certain amount of radiation is irradiated to a stimulable phosphor employable for the method for converting radiographic image of the present invention and then the accumulated energy is eliminated with a tungsten lamp light, and (e) and (f) show, respectively, decay characteristics of accumulated energy when stimulable phosphors, BaFBr:Eu and BaFCl:Eu, employable for the prior art method are measured in the same manner as above.

As apparent from Fig. 2, the stimulable phosphor employable for the method for converting radiographic image of the present invention may exhibit a high decay speed of accumulated energy, which may lead to a more reduced time for eliminating residual image in comparison with the prior art method.

Fig. 3 shows an outlined embodiment wherein a stimulable phosphor represented by the above formula [I] is employed

in the form of a radiation energy storage panel in the present method for converting radiographic image.

In Fig. 3, 11 is a radiation generating apparatus, 12 is the subject, 13 is a radiation energy storage panel which contains a visible or infrared light stimulable phosphor-containing layer having a stimulable phosphor of the above formula [I], 14 is an exciting light source emitting as fluorescence a radiation latent image of the radiation energy storage panel 13, 15 is a photoelectric conversion apparatus for detecting the fluorescence emitted from the radiation energy storage panel 13, 16 is a regenerating apparatus of a photoelectric signal detected with the photoelectric conversion apparatus 15 as image, 17 is an apparatus for representing the regenerated image and 18 is a filter for cutting a reflective light from a light source 14 and transmitting only the light emitted from the radiation energy storage panel 13. Though Fig. 3 shows the case where a radiation transmission image of the subject is to be formed, there is no particular need for the said radiation generating apparatus 11 if the subject 12 itself would emit radiation. Also, the apparatus after the photoelectric conversion apparatus 15 may be any of those wherein photosignal from the panel 13 could be regenerated as image in any form or shape without any limitation to the foregoing solely. As illustrated in fig. 3, when the subject 12 is positioned between the radiation generating apparatus 11 and the radiation energy storage panel 13 and irradiated with radiation, radiation may transmit according to changes in radiation transmittance of each part in the subject 12 and the transmitted image (i.e., image upon strength and weakness of radiation) is entered into the radiation energy storage panel 13. This incident transmitted image is absorbed into a stimulable phosphor-containing layer of the radiation energy storage panel 13, whereby the number of electrons and/or positive

holes could be generated proportionally to the radiation dose absorbed into the stimulable phosphor-containing layer and accumulated in trap level of the stimulable phosphor. Namely, there is formed a latent image having accumulated therein evergy from radiation transmission image. Subsequently, the latent image is actualized by excitation with photo-energy. Namely, the stimulable phosphor-containing layer is irradiated with a light source 14 emitting a light in visible or infrared region to drive out the electron and/or positive hole accumulated in trap level and emit accumulated evergy as fluorescence. Strength and weakness of the emitted fluorescence would be proportional to the number of accumulated electron and/or positive hole, i.e., strength and weakness of radiation evergy absorbed in the stimulable phosphor-containing layer of the radiation energy storage panel 13, the photosignal is converted to electric signal by means of a photoelectric conversion apparatus 15, e.g., a photomultiplier and regenerated as image by means of an image processing apparatus 16 and then the image is represented by means of an image representing apparatus 17. The image processing apparatus 16 is not only to regenerate electric signal simply as image signal but, more effectively, one can use the apparatus capable of accomplishing the so-called image processing, image operation, image memory, image storage and the like.

Also, where excited with photo-energy in the present method, there is a need to separate the reflective light from exciting light from the fluorescence emitted from the stimulable phosphor-containing layer and the photoelectric conversion apparatus receiving fluorescence emitted from the stimulable phosphor-containing layer is generally highly sensitive to photo-energy of a short wave length light of not more than 600 nm, so that fluorescence emitted from the stimulable phosphor-

containing layer may desirably have a spectral distribution within a short wave length region as far as possible. The light emitted from the stimulable phosphor employable for the present method has a wave length region of 300 - 500 nm, while an exciting light has a wave length region of 500 - 900 nm; thus, the above-mentioned conditions may be simultaneously satisfied. More specifically, said stimulable phosphor employable for this invention shows the emission having a main peak of not more than 500 nm, which can be easily separable from an exciting light and coincide well with spectral sensitivity of the receiving apparatus to achieve an effective receipt of light, which can lead to an enhanced sensitivity of an image receiving system.

As the stimulable exciting light source 14 which may be employed for the present method, there may be used a light source involving a stimulable exciting wave length of the stimulable phosphor used for the radiation energy storage panel 13. Particularly, use of laser light may simplify an optical system and, in addition, a stimulable emission efficiency may be enhanced, because of a possible increase in strength of an exciting light, to give more satisfactory results. As the laser, there may be mentioned an He-Ne laser, an He-Cd laser, an Ar ion laser, a Kr ion laser, an N_2 laser, a YAG laser and a second harmonic wave thereof, a ruby laser, a semi-conductor laser, various pigment lasers, a metal vapour laser such as a copper vapour laser and the like. Usually, there may be preferably employed such continuous wave lasers as an He-Ne laser or an Ar ion laser, but there may be also used a pulse-oscillating laser if a scanning time in one image element of panel were synchronized with pulse. Further, where there is applied the method for separation utilizing emission delay as disclosed in Japanese Provisional Patent Publication No. 22046/1984 without using the filter 18, it is rather

preferable to utilize a pulse-oscillating laser than modulation using a continuously oscillating laser.

Among the above-mentioned various laser light sources, a semi-conductor laser is particularly preferable, because it is small-sized and inexpensive and further there is no need to use a modulator.

As the filter 18, it may serve to transmit a stimulable emission emitted from the radiation energy storage panel 13 and cut an exciting light, therefore, it is determined upon a combination of a wave length of the stimulable emission from the stimulable phosphor contained in the radiation energy storage panel 13 with a wave length of the exciting light 14. For instance, in the case of a practically preferable combination of a stimulable exciting wave length 500 - 900 nm with a stimulable emission wave length 300 - 500 nm, there may be used as a filter, for instance, various purple to blue colored glass filters, e.g., C-39, C-40, V-40, V-42 and V-44 (available from Kabushiki Kaisha Toshiba), 7-54 and 7-59 (available from Corning Co., Ltd.), BG-1, BG-3, BG-25, BG-37 and BG-38 (available from Spectrofilm Co., Ltd.) and the like. Also, if an interference filter is applied, there may be selected and applied to some extent a filter having optional characteristics.

As the photoelectric conversion apparatus 15, there may be employed any of those capable of converting change in light amount to change in electric signal, for example, a photoelectric tube, a photomultiplier, a photodiode, a phototransistor, a solar cell, a photoconductive element and the like.

Next, the radiation nergy storage panel, which may be employed for the present method for converting radiographic image, will be illustrated below.

The radiation energy storage panel, as explained above, is composed of a support or base and at least one layer of stimulable phosphor-containing layers containing a stimulable phosphor represented by the above general formula [I], said layer having placed over said support.

Among the stimulable phosphor [I], there may be preferably mentioned, with regard to a stimulable emission luminance, the phosphor of the general formula [I] wherein M^I is preferably at least one alkali metal selected from Li, Na, K, Rb and Cs, more preferably, Rb, Cs, Na containing Rb and/or Cs and K containing Rb and/or Cs, particularly preferably at least one alkali metal selected from Rb and Cs. M^{II} is preferably at least one alkaline earth metal selected from Be, Mg, Ca, Sr, and Ba. M^{III} is preferably at least one trivalent metal selected from Y, La, Lu, Sm, Al, Ga, Gd and In. X, X' and X" are preferably at least one halogen selected from F, Cl and Br. The value a for representing the content of $M^{II}X'_2$ and b for representing the content of $M^{III}X''_3$ are preferably selected from the range of $0 \leqq a < 0.4$ and $0 \leqq b \leqq 10^{-2}$, respectively. Where the value a is $a > 0.5$, it is not preferable, in particular, owing to a rapid decrease in a stimulable emission luminance.

In the above general formula [I], the metal exide A is preferably at least one MgO, Al_2O_3, SiO_2 and TiO_2. The value c for representing the content of A is preferably in the range of $0 \leqq c \leqq 0.2$.

Further, the activator B is preferably at least one metal selected from Eu, Tb, Ce, Tm, Dy, Ho, Gd, Lu, Sm, Y, Tl and Na, particularly preferably at least one metal selected from Eu, Ce, Sm, Tl and Na, more preferably, B comprises at least Tl. Also, the value d for representing an amount of the activator is preferably selected from the range of $10^{-6} \leqq d \leqq 0.1$ in view of a stimulable

emission luminance.

There may be preferably employed the alkali halide phosphor represented by the above formula [I'] in this invention.

The present alkali halide phosphor having the above composition is irradiated with radiation such as an X-ray, an ultra-violet ray, electron beam and the like and then stimulated and excited by irradiation with either or both of visible and infrared lights, whereby a clearly stronger stimulated excitation may occur, as compared with the alkali halide phosphor already known and worked in the same manner as above.

Also, where the present alkali halide phosphor having the above composition is irradiated with radiation such as X-ray, ultra-violet ray, electron beam and the like and then stimulated and excited by irradiation with either or both of visible and infrared lights at a rectangularly variable strength, a better response to stimulable excitation can be realized with a less afterglow of stimulation, as compared with the alkali halide phosphor already known and worked in the same manner as above.

The present stimulable phosphor $(M_{1-x} \cdot M^{I}_{x})X \cdot aM^{II}X'_2 \cdot bM^{III}X''_3 \cdot cA:dB$ can be prepared, e.g., according to the process as described below.

As a raw material for stimulable phosphor, there may be employed:

I) One or more of LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr and CsI;

II) One or more of BeF_2, $BeCl_2$, $BeBr_2$, BeI_2, MgF_2, $MgCl_2$,

$MgBr_2$, MgI_2, CaF_2, $CaCl_2$, $CaBr_2$, CaI_2, SrF2, $SrCl_2$, $SrBr_2$, SrI_2, BaF_2, $BaCl_2$, $BaBr_2$, $BaBr_2 \cdot 2H_2O$, BaI_2, ZnF_2, $ZnCl_2$, $ZnBr_2$, ZnI_2, CdF_2, $CdCl_2$, $CdBr_2$, CdI_2, CuF_2, $CuCl_2$, $CuBr_2$, CuI, NiF_2, $NiCl_2$, $NiBr_2$ and NiI_2;

III) One of more of ScF_3, $ScCl_3$, $ScBr_3$, ScI_3, YF_3, YCl_3, YBr_3, YI_3, LaF_3, $LaCl_3$, $LaBr_3$, LaI_3, CeF_3, CeI_3, $CeBr_3$, CeI_3, PrF_3, $PrCl_3$, $PrBr_3$, PrI_3, NdF_3, $NdCl_3$, $NdBr_3$, NdI_3, PmF_3, $PmCl_3$, $PmBr_3$, PmI_3, SmF_3, $SmCl_3$, $SmBr_3$, SmI_3, EuF_3, $EuCl_3$, $EuBr_3$, EuI_3, GdF_3, $GdCl_3$, $GdBr_3$, GdI_3, TbF_3, $TbCl_3$, $TbBr_3$, TbI_3, DyF_3, $DyCl_3$, $DyBr_3$, DyI_3, HoF_3, $HoCl_3$, $HoBr_3$, HoI_3, ErF_3, $ErCl_3$, $ErBr_3$, ErI_3, TmF_3, $TmCl_3$, $TmBr_3$, TmI_3, YbF_3, $YbCl_3$, $YbBr_3$, YbI_3, LuF_3, $LuCl_3$, $LuBr_3$, LuI_3, AlF_3, $AlCl_3$, $AlBr_3$, AlI_3, GaF_3, $GaCl_3$, $GaBr_3$, GaI_3, InF_3, $InCl_3$, $InBr_3$, InI_3;

IV) An activator material of one or more of Eu compound group, Tb compound group, Ce compound group, Tm compound group, Dy compound group, Pr compound group, Ho compound group, Nd compound group, Yb compound group, Er compound group, Gd compound group, Lu compound group, Sm compound group, Y compound group, Tl compound group, Na compound group, Ag compound group, Cu compound group and Mg compound group; and

V) one or more of BeO, MgO, CaO, SrO, BaO, ZnO, Al_2O_3, Y_2O_3, La_2O_3, In_2O_3, SiO_2, TiO_2, ZrO_2, GeO_2, SnO_2, Nb_2O_5, Ta_2O_5 and ThO_2.

In the case of the phosphor having the formula [I'], there may be employed, as the above-mentioned Tl compound,

VI) One or more of such thallium compounds as TlF, TlCl, TlBr, TlI, Tl_2O, Tl_2O_3 and others.

Raw materials of the above-mentioned stimulable phosphor I) - V) are weighed so as to form a mixture composition of the formula [I]: $(M_{1-x} \cdot M^{I}_{x})X \cdot aM^{II}X'_{2} \cdot bM^{III}X''_{3} \cdot cA:dB$ wherein stoichiometrically

$0 \leqq a \leqq 1$, preferably $0 \leqq a \leqq 0.4$,
$0 \leqq b \leqq 0.5$, preferably $0 \leqq b \leqq 10^{-2}$,
$0 \leqq c \leqq 0.5$, preferably $0 \leqq c \leqq 0.2$, and
$0 < d \leqq 0.2$, preferably $10^{-6} \leqq d \leqq 0.1$,

and then mixed well by means of a mortar, a ball mill, a mixer mill and others.

Then, the resulting stimulable phosphor raw material mixture is charged into a heat-resistant vessel such as a quartz crucible or an alumina crucible and baked in an electric furnace. A baking temperature is suitably 500 to 1000 ^{o}C. A baking period of time may be vaired depending upon an amount of the raw mixture charged, the baking temperature applied and others, but 0.5 - 6 hours may be generally suitable. As a baking atmosphere, there may suitably be applied a weakly oxidative atmosphere such as a nitrogen gas atmosphere containing a small volume of oxygen gas, or a neutral atmosphere such as a nitrogen gas atmosphere, an argon gas atmosphere and the like. Moreover, a radiation luminance of the phosphor may be enhanced by taking out a baked product from the electric furnace after baked one under the above-mentioned baking condition, finely grinding it, charging the baked powder again into a heat resistant vessel, placing in an electric furnace and then annealing under the same baking condition as above. Also, when a baked product is cooled from the baking temperature to room temperature, the desired stimulable phosphor may be obtained by taking out the baked product from the electric furnace and allowing it to be cooled in air; however, a radiation luminance of the stimulable phosphor by stimulation may be more enhanced by cooling the said phosphor under the same weakly oxidative atmosphere or neutral atmosphere as

applied in baking. Further, a radiation luminance of the resultings by stimulation may be far more enhanced by moving the baked product from a heating portion to a cooling portion in an electric furnace to quench the phosphor in a weakly oxidative atmosphere or a neutral atmosphere. Moreover, it is preferable for obtaining said stimulable phosphor raw material as a uniform mixture to prepare said material as an aqueous dispersion, in this instance, the dispersion is dried and then subjected to the above-mentioned baking.

After baking, the resultant stimulable phosphor is finely grinding and subsequently worked according to various procedures commonly adopted for preparing a phosphor such as washing, drying, screening, and so on to afford the stimulable phosphor of this invention.

An average particle diameter of the stimulable phosphor, which may be employed for the present radiation energy storage panel 13, may be optionally selected usually in the range of an average particle diameter of 0.1 - 100 μm, taking into consideration sensitivity and graininess of the radiation energy storage panel 13. More preferably, the phosphor with an average particle size of 1 - 30 μm may be used.

In the present radiation energy storage panel 13, the present stimulable phosphor may be generally dispersed in a suitable binder and coated over a support. As the binder, there may be usually applied those binders employed for laminating such as a protein, e.g., gelatin; a polysaccharide, e.g., dextran or gum arabic; a polyvinyl butyral; a polyvinyl acetate, a cellulose nitrate, an ethyl cellulose, a vinylidene chloride-vinyl chloride copolymer, a poly(methyl methacrylate), a vinyl chloride-vinyl acetate copolymer, a polyurethane, a cellulose acetate butyrate, a polyvinyl alcohol and the like.

Generally, a binder may be employed in the range of 0.01 - 1 part by weight per 1 part by weight of the stimulable phosphor. However, less binder is preferable for sensitivity and sharpness of the resulting radiation energy storage panel 13 and a range of 0.03 - 0.2 part by weight is more preferable in a further view of easiness in coating.

Moreover, there may be henerally placed in the present radiation energy storage panel 13 a protective layer physically or chemically protecting the stimulable phosphor-containing layer over an externally exposed surface of the stimulable phosphor-containing layer (i.e., an uncovered surface at the bottom of the phosphor layer base plate). The protective layer may be formed by direct coating of a coating liquid for the protective layer over the stimulable phosphor-containing layer or by adhesion of the protective layer previously and separately prepared over the stimulable phosphor-containing layer.

As a material for the protective layer, there may be employed those materials commonly used for the protective layer such as a cellulose nitrate, an ethyl cellulose, a cellulose acetate, a polyester, a polyethylene terephthalate and the like.

And further, if a protective layer may transmit a stimulable emission light and irradiation may be done from the protective layer side, there may be selected any of those capable of transmitting an excited light, with a preferable film thickness being approximately 2 - 40 μm.

One embodiment of the preparation of the radiation energy storage panel 13 will be illustrated hereinbelow.

First, a finely grinded stimulable phosphor, a binder and

a solvent are admixed, kneaded well to prepare a coating liqsid having uniformly dispersed therein the stimulable phosphor.

As the above-mentioned solvent, there may be mentioned, for instance, a lower alcohol such as methanol, ethanol, n-propanol, n-butanol and the like; a chlorine-containing hydrocarbon such as methylene chloride, ethylene chloride and the like; a ketone such as acetone, methyl ethyl ketone, methyl isobutyl ketone and the like; a lower ester such as methyl acetate, ethyl acetate, butyl acetate and the like; an ether such as dioxane, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and the like and these solvents may be employed in the form of a mixture thereof.

There may be further incorporated therein a wide variety of useful additives such as a dispersing agent to supplement dispersibility of the stimulable phosphor in a coating liquid, a plasticizer to ensure adhesion of the said phosphor particles with said binder after coating and drying.

As the dispersing agent, there may be mentioned, for example, phthalic acid, stearic acid, caproic acid or a lipophilic surface active agent and the like.

As the plasticizer, there may be mentioned, for example, a phosphoric acid ester such as triphenyl phosphate, tricresyl phosphate, diphenyl phosphate and the like; a phthalic acid ester such as diethyl phthalate, dimethoxyethyl phthalate and the like; a glycolic acid ester such ethyl phthalylethyl glycolate, butyl phthalylbutyl glycolate and the like; a polyethylene glycol-dibasic aliphatic acid polyester such as triethylene glycol-adipic acid polyester, diethylene glycol-succinic acid polyester and the like; and others.

The coating liquid prepared as above may be uniformly coated over a support according to any coating methods commonly applied such as a roll coater method, a blade docter method and so on to form the stimulable phosphor-containing layer.

As the support or base which may be employed for this invention, there may be mentioned, for example, various synthetic resin sheets (e.g., sheets of a cellulose acetate, a polyester, a polyethylene terephthalate, a polyamide, a polyimide, a triacetate, a polycarbonate and the like), various metallic sheets (e.g., sheets of aluminum, aluminum alloy and the like), various paper sheets (e.g., sheets of baryta paper, resin coated paper, pigment paper and the like), various glass sheets and others.

A dry thickness of said stimulable phosphor-containing layer may be varied depending upon the purpose of utilization of the radiation energy storage panel as well as the sort of the stimulable phosphor, the proportion of the binder to the stimulable phosphor; a thickness of 10 μm to 1000 μm is suitable with 80 μm to 600 μm being preferable.

Still further, it may be suitable for increasing image sharpness formed in the radiation energy storage panel 13 to have dispersed a white powder in the stimulable phosphor-containing layer as disclosed, for instance, in Japanese Provisional Patent Publication No. 146447/1980, or it may be also suitable for increasing image sharpness of the stimulable phosphor-containing layer or absorbing a stimulable exciting light to make a proper coloration by having dispersed in the stimulable phosphor-containing layer a coloring agent capable of absorbing a stimulable exciting light as disclosed, for example in Japanese Provisional Patent Publication No. 163500/1980. Addi-

tionally, in order to improve sharpness and sensitivity of the radiation energy storage panel 13, it may be suitable to place a photoreflective layer between the base and the stimulable phosphor-containing layer as disclosed in Japanese Provisional Patent Publication No. 11393/1981.

In the present radiation energy storage panel, the phosphor layer may be provided over the support according to other methods, e.g., vacuum evaporation coating or sputtering than the above-mentioned coating methods. In this case, there is no need to apply a binder so that a packed density of the stimulable phosphor may be increased and one can obtain a favourable radiation energy storage panel with regard to sensitivity and resolving power thereof.

In Fig. 4, there is illustrated an emission spectrum from stimulation of the so-obtained phosphor of the formula [I], $(M_{1-x} \cdot M^{I}_{x})X \cdot aM^{II}X'_2 \cdot bM^{III}X''_3 \cdot cA:dB$ according to this invention. Its practical formulation is as defined below.

(a) $RbBr \cdot 0.05BaFBr \cdot 0.01AlF_3:0.001Eu$
(b) $0.99RbBr \cdot 0.01CsF \cdot 0.05BaFCl \cdot 0.01LaF_3:0.001Tl$
(c) $CsBr \cdot 0.05BaFCl \cdot 0.01YF_3:0.002Tl$

These stimulable phosphors are irradiated with an X-ray of 80 KVp and the emission spectrum as shown is measured by exciting said phosphor with a semi-conductor laser having an oscillating wave length of 780 nm.

Also, Fig. 5 illustrates an excited spectrum of the present phosphor $M^{I}X \cdot aM^{II}X'_2 \cdot bM^{III}X''_3:cA$ by stimulation. Namely, said spectrum is an excited spectrum of each of the above-mentioned stimulable phosphors (a), (b) and (c) by stimulation.

On the other hand, Figs. 6 and 7 illustrate stimulable emission spectra of the present phosphors represented by the formula [I'], $(M_{1-x} \cdot M^{I}_{x})X \cdot aM^{II}X'_2 \cdot bM^{III}X''_2:cTl:dA$, respectively. Their practical formulations are as defined below.

(d) $0.98CsBr \cdot 0.02RbI:0.002Tl$

(e) $0.97RbBr \cdot 0.03CsF:0.002Tl$

Namely, said phosphors are irradiated with X-ray of 80 KVp and the emission spectrum as shown is measured by exciting said phosphor with a semi-conductor laser having an oscillating wave length of 780 nm.

Further, Figs. 8 and 9 show the stimulable emission spectra of the present phosphors, $(M_{1-x} \cdot M^{I}_{x})X \cdot aM^{II}X'_2 \cdot bM^{III}X''_2:cTl:dA$, which spectra are stimulable excited spectra of said phosphors irradiated with X-ray of 80 KVp.

Examples

This invention will be more fully illustrated by way of the following examples.

Example 1

Each of stimulable phosphor raw materials was weighed as shown below with the items (1) - (53) and admixed well by means of a ball mill to prepare 53 kinds of mixtures of phosphor materials.

(1)	RbBr	163.7 g	(0.99 mole)
	CsF	1.52 g	(0.01 mole)
	TlBr	0.284 g	(0.001 mole)
(2)	CsBr	210.7 g	(0.99 mole)
	CsF	1.52 g	(0.01 mole)
	TlBr	0.284 g	(0.001 mole)

(3)	RbBr	82.7 g	(0.5 mole)
	CsBr	106.4 g	(0.5 mole)
	CsF	1.52 g	(0.01 mole)
	TlBr	0.284 g	(0.001 mole)
(4)	RbCl	120.9 g	(1 mole)
	CaF_2	7.81 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(5)	RbBr	165.4 g	(1 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(6)	RbBr	165.4 g	(1 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
	Tb_4O_7	0.0748 g	(0.0001 mole)
(7)	RbBr	165.4 g	(1 mole)
	TlBr	0.284 g	(0.001 mole)
(8)	RbBr	165.4 g	(1 mole)
	TlBr	0.284 g	(0.001 mole)
	NaBr	0.0206 g	(0.0002 mole)
(9)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	TlBr	0.284 g	(0.001 mole)
(10)	RbBr	157.1 g	(0.95 mole)
	CsF	7.60 g	(0.05 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(11)	RbBr	157.1 g	(0.95 mole)
	LiI	6.69 g	(0.05 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	Tl_2O_3	0.228 g	(0.0005 mole)
(12)	RbI	212.4 g	(1 mole)
	MgF_2	62.31 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)

(13)	CsF	151.9 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	LaF_2	1.96 g	(0.01 mole)
	EuF_3	0.209 g	(0.001 mole)
(14)	CsBr	212.8 g	(1 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(15)	CsBr	212.8 g	(1 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(16)	CsBr	212.8 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(17)	CsBr	212.8 g	(1 mole)
	$BaBr_2$	29.71 g	(0.1 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(18)	CsBr	212.8 g	(1 mole)
	YCl_3	0.976 g	(0.005 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(19)	CsBr	212.8 g	(1 mole)
	YCl_3	19.53 g	(0.1 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(20)	CsBr	212.8 g	(1 mole)
	YCl_3	78.11 g	(0.4 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(21)	NaI	149.9 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	YF_3	1.464 g	(0.01 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(22)	KBr	119.0 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(23)	KI	166.0 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(24)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)

	$BaBr_2 \cdot 2H_2O$	33.31 g	(0.1 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(25)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	$BaBr_2 \cdot 2H_2O$	33.31 g	(0.1 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(26)	RbBr	165.4 g	(1 mole)
	BaF_2	26.31 g	(0.15 mole)
	$BaBr_2 \cdot 2H_2O$	49.97 g	(0.15 mole)
	Tl_2O	0.424 g	(0.001 mole)
(27)	RbBr	165.4 g	(1 mole)
	BaF_2	26.31 g	(0.15 mole)
	$BaCl_2$	31.23 g	(0.15 mole)
	NaF	0.0084 g	(0.0002 mole)
(28)	TbI	212.4 g	(1 mole)
	MgF_2	62.31 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	Eu_2O_3	0.176 g	(0.0005 mole)
(29)	CsBr	212.8 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	$BaBr_2$	29.71 g	(0.1 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(30)	CsBr	212.8 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	Tl_2O	0.212 g	(0.0005 mole)
(31)	RbBr	160.4 g	(0.97 mole)
	CsF	4.56 g	(0.03 mole)
	TlBr	0.0568 g	(0.0002 mole)
(32)	RbBr	160.4 g	(0.97 mole)
	CsF	4.56 g	(0.03 mole)
	TlBr	0.568 g	(0.002 mole)
(33)	RbBr	160.4 g	(0.97 mole)
	CsF	4.56 g	(0.03 mole)
	TlBr	5.68 g	(0.02 mole)
(34)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)

	AlF_3	0.840 g	(0.01 mole)
	TlBr	0.568 g	(0.002 mole)
(35)	RbBr	157.1 g	(0.95 mole)
	CsF	7.60 g	(0.05 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	Tl_2O	0.424 g	(0.001 mole)
(36)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	TlBr	0.568 g	(0.002 mole)
	NaBr	0.0412 g	(0.0004 mole)
(37)	RbI	212.4 g	(1 mole)
	MgF_2	6.23 g	(0.1 mole)
	LaF_3	1.96 g	(0.01 mole)
	AgI	0.470 g	(0.002 mole)
(38)	CsF	151.9 g	(1 mole)
	TlF	0.447 g	(0.002 mole)
(39)	CsBr	212.8 g	(1 mole)
	NaBr	0.0206 g	(0.0002 mole)
(40)	CsBr	212.8 g	(1 mole)
	NaBr	0.206 g	(0.002 mole)
(41)	CsBr	212.8 g	(1 mole)
	NaBr	2.06 g	(0.02 mole)
(42)	CsBr	212.8 g	(1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	NaBr	0.206 g	(0.002 mole)
(43)	CsBr	202.2 g	(0.95 mole)
	RbI	10.62 g	(0.05 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	NaBr	0.206 g	(0.002 mole)
(44)	CsBr	208.5 g	(0.98 mole)
	RbI	4.25 g	(0.02 mole)
	TlBr	0.568 g	(0.002 mole)

(45)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	SiO_2	0.601 g	(0.01 mole)
	TlBr	0.568 g	(0.002 mole)
(46)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	SiO_2	3.004 g	(0.05 mole)
	TlBr	0.568 g	(0.002 mole)
(47)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	SiO_2	6.009 g	(0.1 mole)
	TlBr	0.568 g	(0.002 mole)
(48)	RbBr	165.4 g	(1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	SiO_2	24.03 g	(0.4 mole)
	TlBr	0.568 g	(0.002 mole)
(49)	CsBr	212.8 g	(1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	Al_2O_3	1.020 g	(0.01 mole)
	NaBr	0.206 g	(0.002 mole)
(50)	CsBr	212.8 g	(1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	Al_2O_3	5.098 g	(0.05 mole)
	NaBr	0.206 g	(0.002 mole)
(51)	CsBr	212.8 g	(1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	Al_2O_3	10.20 g	(0.1 mole)
	NaBr	0.206 g	(0.002 mole)
(52)	CsBr	212.8 g	(1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)

	YF_3	1.46 g	(0.01 mole)
	Al_2O_3	40.78 g	(0.4 mole)
	NaBr	0.206 g	(0.002 mole)
(53)	RbI	212.4 g	(1 mole)
	MgF_2	62.31 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	MgO	2.016 g	(0.05 mole)
	EuI_3	0.533 g	(0.001 mole)

Then, the above 53 kinds of the stimulable phosphor mixtures were packed into a quartz boat and baked in an electric furnace, respectively. Baking was carried out at 650 ^{o}C for 2 hours under stream of nitrogen gas at a flow rate of 2500 cc/min and then the baked product was allowed to cool up to room temperature.

The resulting baked product was finely grinded by means of a ball mill and passed through a sieve with 150 mesh for regulating a particle diameter, thereby yielding the respective stimulable phosphors.

Then, radiation energy storage panels of the present invention were prepared by using said 53 kinds of the stimulable phosphors. Each of the radiation energy storage panel was prepared as follows.

First, 8 parts by weight of a stimulable phosphor were dispersed in 1 part by weight of polyvinyl butyral (a binder) by using a solvent composed of a mixture of equal volumes of acetone and ethyl acetate, and the resulting dispersion was uniformly coated over a polyethylene telephthalate film (a support) kept horizontally by using a wire bar and allowed to natural seasoning, thereby forming a radiation energy storage panel of the present invention having film thickness of about 300 μm.

These 53 kinds of the radiation energy storage panels of the present invention were each irradiated with X-ray having a tube voltage of 80 KVp and a tube current of 100 mA for 0.1 second at a distance of 100 cm from the focus of an X-ray tube and then excited with a semi-conductor laser of 780 nm and 10 mW. Fluorescence emitted by stimulation from the stimulable phosphor-containing layer was measured by means of a photodetector. The results are summarized in Table 1.

Comparative Example 1

Following the same procedures as in Example 1 except that 175.4 g (1 mole) of BaF_2, 333.3 g (1 mole) of $BaBr_2 \cdot 2H_2O$ and 0.352 g (0.001 mole) of Eu_2O_3 were used as a raw material for stimulable phosphor, there was obtained a stimulable phosphor BaFBr:0.001Eu. A comparative radiation energy storage panel was prepared from the stimulable phosphor in the same manner as in Example 1 and a stimulable emission luminance was measured by using a semi-conductor laser (780 nm, 10 mW). The results are also shown in Table 1.

Comparative Example 2

Following the same procedures as in Comparative Example 1 except that an He-Ne laser (633 nm, 10 mW) was applied instead of the semi-conductor laser, one measured stimulable emission luminance. The results are also shown in Table 1.

Reference Example 1

Following the exactly same procedures as in Example 1 except that the metal oxide components SiO_2, Al_2O_3, MgO and TiO_2 were omitted in turn from the raw materials of stimulable phosphor samples of Example 1 (45), (49), (52)

and (53), respectively, there were prepared the following reference samples (1), (2), (3) and (4) corresponding to the samples (1), (5), (9) and (10), the stimulable emission luminance of which was measured by means of a semi-conductor laser (780 nm, 10 mW). The results are also shown in Table 1.

Reference sample (1): $RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3 : 0.002Tl$
Reference sample (2): $CsBr \cdot 0.1BaCl_2 \cdot 0.01YF_3 : 0.002Na$
Reference sample (3): $RbI \cdot 0.1MgF_2 \cdot 0.01AlF_3 : 0.001Eu$

Table 1

	Composition of phosphor	Exciting wave length	Relative emission strength by stimulation
Comparative example 1	BaFBr:Eu	780 nm	1
Comparative example 2	BaFBr:Eu	633 nm	38
Example 1 (1)	$0.99RbBr \cdot 0.01CsF \cdot 0.001Tl$	780 nm	300
Example 1 (2)	$0.99CsBr \cdot 0.01CsF \cdot 0.001Tl$	780 nm	120
Example 1 (3)	$0.5RbBr \cdot 0.5CsBr \cdot 0.01CsF : 0.001Tl$	780 nm	250
Example 1 (4)	$RbCl \cdot 0.1CaF_2 \cdot 0.01AlF_3 : 0.001Eu$	780 nm	62
Example 1 (5)	$RbBr : 0.001Eu$	780 nm	80
Example 1 (6)	$RbBr : 0.001Eu \cdot 0.0004Tb$	780 nm	88
Example 1 (7)	$RbBr : 0.001Tl$	780 nm	96
Example 1 (8)	$RbBr : 0.001Tl \cdot 0.0002Na$	780 nm	102
Example 1 (9)	$RbBr : 0.1BaF_2 \cdot 0.01AlF_3 : 0.001Tl$	780 nm	110
Example 1(10)	$0.95RbBr \cdot 0.05CsF \cdot 0.1BaF_2 \cdot 0.01AlF_3 : 0.001Tl$	780 nm	205
Example 1(11)	$0.95RbBr \cdot 0.5LiI \cdot 0.1BaF_2 \cdot 0.01AlF_3 : 0.001Tl$	780 nm	180
Example 1(12)	$RbI \cdot 0.1MgF_2 \cdot 0.01AlF_3 : 0.001Eu$	780 nm	72

Table 1 (Cont'd)

	Composition of phosphor	Exciting wave length	Relative emission strength by stimulation
Example 1(13)	$CsF \cdot 0.1BaF_2 \cdot 0.01LaF_3$: 0.001Eu	780 nm	60
Example 1(14)	CsBr:0.001Eu	780 nm	72
Example 1(15)	CsBr:0.001Tl	780 nm	88
Example 1(16)	$CsBr \cdot 0.1BaBr_2$:0.001Tl	780 nm	98
Example 1(17)	$CsBr \cdot 0.4BaBr_2$:0.001Tl	780 nm	90
Example 1(18)	$CsBr \cdot 0.005YCl_3$:0.001Tl	780 nm	112
Example 1(19)	$CsBr \cdot 0.1YCl_3$:0.001Tl	780 nm	96
Example 1(20)	$CsBr \cdot 0.4YCl_3$:0.001Tl	780 nm	90
Example 1(21)	$NaI \cdot 0.1BaF_2 \cdot 0.01YF_3$: 0.001Eu	780 nm	56
Example 1(22)	$KBr \cdot 0.1BaF_2 \cdot 0.01YF_3$: 0.001Eu	780 nm	50
Example 1(23)	$KI \cdot 0.1BaF_2 \cdot 0.01AlF_3$: 0.001Eu	780 nm	58
Example 1(24)	RbBr•0.2BaFBr:0.001Eu	780 nm	82
Example 1(25)	RbBr•0.2BaFBr:0.001Tl	780 nm	92
Example 1(26)	RbBr•0.3BaFBr:0.002Tl	780 nm	90
Example 1(27)	RbBr•0.3BaFCl:0.0002Na	780 nm	66
Example 1(28)	$RbI \cdot 0.1MgF_2 \cdot 0.01AlF_3$: 0.001Eu	780 nm	72
Example 1(29)	CsBr•0.2BaFBr:0.001Tl	780 nm	100
Example 1(30)	CsBr•0.2BaFCl:0.001Tl	780 nm	94
Example 1(31)	0.97RbBr•0.03CsF•0.0002Tl	780 nm	124
Example 1(32)	0.97RbBr•0.03CsF•0.002Tl	780 nm	196
Example 1(33)	0.97RbBr•0.03CsF•0.02Tl	780 nm	118
Example 1(34)	$RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3$: 0.002Tl	780 nm	116
Example 1(35)	$0.95RbBr \cdot 0.05CsF \cdot 0.1BaF_2 \cdot 0.01AlF_3$:0.002Tl	780 nm	205
Example 1(36)	$RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3$: 0.002Tl•0.0004Na	780 nm	133
Example 1(37)	$RbI \cdot 0.1MgF_2 \cdot 0.01LaF_3$: 0.002Ag	780 nm	53

Table 1 (Cont'd)

	Composition of phosphor	Exciting wave length	Relative emission strength by stimulation
Example 1(38)	$CsF:0.002Tl$	780 nm	75
Example 1(39)	$CsBr:0.0002Na$	780 nm	55
Example 1(40)	$CsBr:0.002Na$	780 nm	82
Example 1(41)	$CsBr:0.02Na$	780 nm	61
Example 1(42)	$CsBr:0.1BaCl_2 \cdot 0.01YF_3:0.002Na$	780 nm	90
Example 1(43)	$0.95CsBr \cdot 0.05RbI \cdot 0.1BaCl_2 \cdot 0.01YF_3:0.002Na$	780 nm	157
Example 1(44)	$0.98CsBr \cdot 0.02RbI:0.002Tl$	780 nm	180
Reference Example (1)	$RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.002Tl$	780 nm	104
Example 1(45)	$RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.01SiO_2:0.002Tl$	780 nm	152
Example 1(46)	$RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.05SiO_2:0.002Tl$	780 nm	145
Example 1(47)	$RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.1SiO_2:0.02Tl$	780 nm	121
Example 1(48)	$RbBr \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.4SiO_2:0.002Tl$	780 nm	107
Reference Example (2)	$CsBr:0.1BaCl_2 \cdot 0.01YF_3:0.002Na$	780 nm	88
Example 1(49)	$CsBr:0.1BaCl_2 \cdot 0.01YF_3 \cdot 0.01Al_2O_3:0.002Na$	780 nm	131
Example 1(50)	$CsBr:0.1BaCl_2 \cdot 0.01YF_3 \cdot 0.05Al_2O_3:0.002Na$	780 nm	123
Example 1(51)	$CsBr:0.1BaCl_2 \cdot 0.01YF_3 \cdot 0.1Al_2O_3:0.002Na$	780 nm	101
Example 1(52)	$CsBr:0.1BaCl_2 \cdot 0.01YF_3 \cdot 0.4Al_2O_3:0.002Na$	780 nm	94
Reference Example (3)	$RbI \cdot 0.1MgF_2 \cdot 0.01AlF_3:0.001Eu$	780 nm	73
Example 1(53)	$RbI \cdot 0.1MgF_2 \cdot 0.01AlF_3 \cdot 0.05MgO:0.001Eu$	780 nm	96

As apparent from the above Table 1, the present radiation energy storage panel as prepared from the stimulable phosphors of the above samples (1) to (53) showed a higher emission luminance by stimulation than the one of comparative radiation energy storage panel as measured under the same conditions, said comparative panel being prepared from the prior art stimulable phosphor BaFBr:Eu as shown in the above Comparative Example 1 and hence the method for converting radiographic image of this invention using the present radiation energy storage panel showed a higher sensitivity than the prior art method for converting radiographic image did using the comparative radiation energy storage panel.

Then, the prior stimulable phosphor BaFBr:Eu as seen in Comparative Example 1 showed a peak wave length at approximately 600 nm in the stimulable excited spectrum and it is said that He-Ne laser light (633 nm) was particularly preferable as an exciting light source [see Japanese Provisional Patent Publication No. 15025/1980 and others]. Accordingly, the comparative radiation energy storage panel prepared from BaFBr:Eu was measured for the said stimulable emission luminance under the same conditions as used in the above-mentioned method except that an He-Ne laser (633 nm) was used instead of the semi-conductor laser (780 nm). The results in terms of Comparative Example 2 were shown in the above Table 1, which revealed that the comparative radiation energy storage panel showed a lower stimulable emission luminance than these by all present radiation energy storage panels. Therefore, the present method for converting radiographic image using the present radiation energy storage panel can utilize as an exciting light source a semi-conductor laser so that the present method may be effected in a more miniaturized state with a higher sensitivity, as compared with the prior method for converting radiographic image using the He-Ne laser.

Example 2

Each phosphor raw material was weighed as shown in the following items (54) to (85) and admixed well by means of a ball mill to prepare 35 kinds of mixtures of phosphor raw materials.

(54)	CsBr	202.2 g	(0.95 mole)
	CsI	12.99 g	(0.05 mole)
	TlBr	0.568 g	(0.002 mole)
(55)	CsBr	202.2 g	(0.95 mole)
	CsI	12.99 g	(0.05 mole)
	TlBr	0.568 g	(0.002 mole)
	NaBr	0.0412 g	(0.0004 mole)
(56)	CsBr	202.2 g	(0.95 mole)
	CsI	12.99 g	(0.05 mole)
	TlBr	0.568 g	(0.002 mole)
	AgBr	0.0751 g	(0.0004 mole)
(57)	CsBr	202.2 g	(0.95 mole)
	CsI	12.99 g	(0.05 mole)
	TlBr	0.568 g	(0.002 mole)
	Eu_2O_3	0.0704 g	(0.0002 mole)
(58)	CsBr	206.4 g	(0.97 mole)
	RbI	6.372 g	(0.03 mole)
	TlBr	0.568 g	(0.002 mole)
(59)	CsBr	191.5 g	(0.9 mole)
	RbI	21.24 g	(0.1 mole)
	TlBr	0.568 g	(0.002 mole)
(60)	CsBr	106.4 g	(0.5 mole)
	RbI	106.2 g	(0.5 mole)
	TlBr	0.568 g	(0.002 mole)
(61)	CsBr	191.5 g	(0.9 mole)
	RbI	21.24 g	(0.1 mole)
	BaF_2	17.54 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	TlBr	0.568 g	(0.002 mole)

(62)	CsBr	191.5 g	(0.9 mole)
	RbI	21.24 g	(0.1 mole)
	BaF_2	17.54 g	(0.1 mole)
	LaF_3	1.96 g	(0.01 mole)
	Tl_2O	0.424 g	(0.001 mole)
(63)	CsBr	191.5 g	(0.9 mole)
	NaI	14.99 g	(0.1 mole)
	TlBr	0.568 g	(0.002 mole)
(64)	CsBr	191.5 g	(0.9 mole)
	NaI	14.99 g	(0.1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	TlBr	0.568 g	(0.002 mole)
(65)	CsBr	191.5 g	(0.9 mole)
	KBr	11.90 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(66)	CsBr	191.5 g	(0.9 mole)
	NaCl	5.84 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(67)	CsBr	191.5 g	(0.9 mole)
	LiF	2.59 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(68)	CsCl	151.5 g	(0.9 mole)
	LiF	2.59 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(69)	RbBr	165.4 g	(1 mole)
	TlBr	0.568 g	(0.002 mole)
(70)	RbBr	165.4 g	(1 mole)
	TlBr	0.568 g	(0.002 mole)
	NaBr	0.0412 g	(0.0004 mole)
(71)	RbBr	165.4 g	(1 mole)
	TlBr	0.568 g	(0.002 mole)
	AgBr	0.0751 g	(0.0004 mole)
(72)	RbBr	165.4 g	(1 mole)
	TlBr	0.568 g	(0.002 mole)
	Eu_2O_3	0.0704 g	(0.0002 mole)

(73)	RbBr	160.4 g	(0.97 mole)
	CsF	4.56 g	(0.03 mole)
	TlBr	0.568 g	(0.002 mole)
(74)	RbBr	148.9 g	(0.9 mole)
	CsF	15.19 g	(0.1 mole)
	TlBr	0.568 g	(0.002 mole)
(75)	RbBr	115.8 g	(0.7 mole)
	CsF	45.57 g	(0.3 mole)
	TlBr	0.568 g	(0.002 mole)
(76)	RbBr	148.9 g	(0.9 mole)
	CsF	15.19 g	(0.1 mole)
	BaF_2	17.54 g	(0.1 mole)
	AlF_3	0.840 g	(0.01 mole)
	TlBr	0.568 g	(0.002 mole)
(77)	RbBr	148.9 g	(0.9 mole)
	CsF	15.19 g	(0.1 mole)
	$BaCl_2$	20.82 g	(0.1 mole)
	YF_3	1.46 g	(0.01 mole)
	Tl_2O	0.424 g	(0.001 mole)
(78)	RbBr	148.9 g	(0.9 mole)
	CsI	25.98 g	(0.1 mole)
	TlBr	0.568 g	(0.002 mole)
(79)	RbBr	148.9 g	(0.9 mole)
	RbI	21.24 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(80)	RbBr	148.9 g	(0.9 mole)
	RbI	21.24 g	(0.1 mole)
	BaF_2	17.54 g	(0.1 mole)
	LaF_3	1.96 g	(0.01 mole)
	TlBr	0.568 g	(0.002 mole)
(81)	RbBr	148.9 g	(0.9 mole)
	KBr	11.90 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(82)	RbBr	148.9 g	(0.9 mole)
	NaCl	5.84 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)

(83)	RbBr	148.9 g	(0.9 mole)
	LiF	2.59 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(84)	RbF	85.02 g	(0.9 mole)
	CsBr	21.28 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)
(85)	RbCl	108.8 g	(0.9 mole)
	LiF	2.59 g	(0.1 mole)
	Tl_2O	0.424 g	(0.001 mole)

Then, the above 32 kinds of mixtures of phosphor raw materials were packed in a quartz boat and baked in an electric furnace. Baking was carried out at 650 ^oC for 2 hours under nitrogen gas stream at a flow rate of 2500 cc/min and then the baked product was allowed to cool up to room temperature.

The resulting baked product was finely grinded by means of a ball mill and passed through a sieve with 150 mesh for arranging particle size to give the phosphor samples (54) to (85).

The phosphor samples (54) to (85) were packed into a measurement holder, respectively, and each holder was irradiated with X-ray having a tube voltage of 80 KVp and a tube current of 100 mA for 0.1 second at as distance of 100 cm from the focus of the X-ray tube and then excited with an He-Ne laser light of 10 mW (633 nm, 10 nm) and fluorescence emitted by stimulation from the phosphor was measured by means of a photodetector. The results are shown in Table 2.

Comparative Example 3

Following the same procedures as in Exmaple 2 except that 74.56 g (1 mole) of KCl and 0.424 g (0.001 mole) of Tl_2O were used as a phosphor raw material, there was obtained a phosphor KCl:0.002Tl. In the same manner as in Example 2, a comparative sample (3) was prepared from said phosphor material and a stimulable emission luminance was measured by means of an He-Ne laser (633 nm, 10 mW). The results are also shown in Table 2.

Table 2

	Composition of phosphor	Emission luminance by stimulation λex=633nm
Comparative sample (3)	KCl:0.002Tl	1
Sample (54)	0.95CsBr·0.05CsI:0.002Tl	122
Sample (55)	0.95CsBr·0.05CsI:0.002Tl·0.0004Na	146
Sample (56)	0.95CsBr·0.05CsI:0.002Tl·0.0004Ag	137
Sample (57)	0.95CsBr·0.05CsI:0.002Tl·0.0004Eu	143
Sample (58)	0.97CsBr·0.03RbI:0.002Tl	153
Sample (59)	0.9CsBr·0.1RbI:0.002Tl	102
Sample (60)	0.7CsBr·0.3RbI:0.002Tl	78
Sample (61)	0.9CsBr·0.1RbI·0.1BaF_2·0.01YF_3:0.002Tl	118
Sample (62)	0.9CsBr·0.1RbI·0.1BaF_2·0.01LaF_3:0.002Tl	113
Sample (63)	0.9CsBr·0.1NaI:0.002Tl	86
Sample (64)	0.9CsBr·0.1NaI·0.1$BaCl_2$·0.01AlF_3:0.002Tl	92
Sample (65)	0.9CsBr·0.1KBr:0.002Tl	72
Sample (66)	0.9CsBr·0.1NaCl:0.002Tl	68
Sample (67)	0.9CsBr·0.1LiF:0.002Tl	73

Table 2 (Cont'd)

	Composition of phosphor	Emission luminance by stimulation λex=633nm
Sample (68)	$0.9CsCl \cdot 0.1LiF:0.002Tl$	59
Sample (69)	$RbBr:0.002Tl$	80
Sample (70)	$RbBr:0.002Tl \cdot 0.0004Na$	91
Sample (71)	$RbBr:0.002Tl \cdot 0.0004Ag$	88
Sample (72)	$RbBr:0.002Tl \cdot 0.0004Eu$	96
Sample (73)	$0.97RbBr \cdot 0.03CsF:0.002Tl$	205
Sample (74)	$0.9RbBr \cdot 0.1CsF:0.002Tl$	176
Sample (75)	$0.7RbBr \cdot 0.3CsF:0.002Tl$	124
Sample (76)	$0.9RbBr \cdot 0.1CsF \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.002Tl$	188
Sample (77)	$0.9RbBr \cdot 0.1CsF \cdot 0.1BaCl_2 \cdot 0.01YF_3:0.002Tl$	185
Sample (78)	$0.9RbBr \cdot 0.1CsI:0.002Tl$	147
Sample (79)	$0.9RbBr \cdot 0.1RbI:0.002Tl$	142
Sample (80)	$0.9RbBr \cdot 0.1RbI \cdot 0.1BaF_2 \cdot 0.01LaF_3:0.002Tl$	150
Sample (81)	$0.9RbBr \cdot 0.1KBr:0.002Tl$	115
Sample (82)	$0.9RbBr \cdot 0.1NaCl:0.002Tl$	108
Sample (83)	$0.9RbBr \cdot 0.1LiF:0.002Tl$	121
Sample (84)	$0.9RbF \cdot 0.1CsBr:0.001Tl$	80
Sample (85)	$0.9RbCl \cdot 0.1LiF:0.001Tl$	75

As apparent from Table 2, an emission luminance by stimulation of the above phosphor samples (54) to (85) showed a higher value, as compared with the value measured under the same conditions for the comparative sample (3) composed of the prior phosphor $KCl:0.002Tl$ as shown in Comparative Example 3.

Example 3

The present radiation energy storage panel using the stimulable phosphors (10) and (35) as prepared by Example 1 was irradiated with an X-ray and then with an He-Ne laser for 10 μsec as an exciting light with a rectangularly variable strength. Change in luminance of the stimulable emission from the stimulable phosphor-containing layer was measured by means of a photodetector. Times required for luminance changing from 10 % to up to 90 % in stimulable emission were determined as response speed for exciting light of the stimulable phosphor and the results are shown in Table 3.

Comparative Example 4

Following the same procedures as in Example 3 except that the comparative radiation energy storage panel prepared in Comparative Example 1 was applied instead of the present radiation energy storage panel (10), there was determined response speed. The results are shown in Table 3.

Table 3

	Composition of phosphor	Response speed (μsec)
Sample (10)	$0.95RbBr \cdot 0.05CsF \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.001Tl$	0.7
Sample (35)	$0.95RbBr \cdot 0.05CsF \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.002Tl$	0.7
Comparative Exmaple 4	BaFBr:Eu	2.0

As apparent from Table 3, the present stimulable phosphor showed an approximately 3 times higher response speed, as compared with the comparative stimulable phosphor and the present method for converting radiographic image using the present stimulable phosphor can provide a reading speed of a radiation image as high as 3 times, as compared with the method using the prior stimulable phosphor.

Example 4

The present radiation energy storage panel employed in Example 3 was irradiated with an X-ray in the same manner as in Example 1 and then accumulated energy was eliminated with a halogen lump having 10,000 luxes over 10 seconds. Then, the panel was excited with an He-Ne laser (10 mW) and a stimulable emission luminance from the stimulable phosphor-containing layer was measured by means of a photodetector. the measured results are shown in Table 4 in terms of the emission luminance before elimination with halogen lump as defined 1.

Comparative Example 5

Following the same procedures as in Example 4 except that the comparative radiation energy storage panel prepared by Comparative Example 1 was used instead of the radiation energy storage panel, there was measured stimulable emission luminance. The results as measured are shown in Table 4 wherein the emission luminance before elimination with a halogen lump is defined as 1 in the same manner as in Example 4.

Table 4

	Composition of phosphor	Emission luminance
Sample (10)	$0.95RbBr \cdot 0.05CsF \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.001Tl$	5.1×10^{-3}
Sample (35)	$0.95RbBr \cdot 0.05CsF \cdot 0.1BaF_2 \cdot 0.01AlF_3:0.002Tl$	5.1×10^{-3}
Comparative Exmaple 5	BaFBr:Eu	2.0×10^{-2}

As apparent from Table 4, the present stimulable phosphor can show an approximately 4 times higher elimination speed of the accumulated energy (residual image) in comparison with that of the prior stimulable phosphor. Thus, the present method for converting radiographic image using the present stimulable phosphor can reduce a time for eliminating after image to 1/4, as compared with the comparative stimulable phosphor.

Example 5

The radiation energy storage panels using the present stimulable phosphor, the sample (47) prepared in Example 1 and using the stimulable phosphor prepared in Comparative Example 1 were placed in a humid room set at 50 °C and a relative humidity of 90 % for a forced humidity test. This forced deterioration rate is at least 80 times, as compared with that seen generally in an air-conditioned X-ray chamber at 20 °C and a relative humidity of 50 %. Respective radiation energy storage panels were periodically taken out, irradiated with X-ray in the same manner as in Example 1, excited with a semi-conductor laser and then emission luminance by stimulation was measured at that time. An emission luminance by stimulation in the respective radiation energy storage panels is defined as 100 prior to the

forced humidity test and represented in terms of a relative luminance thereto. Comparison of lowered emission luminances by stimulation with lapse of time was made and the results are shown in Fig. 10.

As apparent from Fig. 10, the radiation energy storage panel using the present stimulable phosphor is superior in water vapor resistance to the panel using the comparative stimulable phosphor and can greatly improve lowering in stimulable emission luminance with lapse of time.

As explained hereinabove, the present stimulable phosphor can provide a remarkably increased emission luminance by stimulation, when irradiated with radiation and then stimulated and excited with either or both or visible ray and infrared ray, as compared with the prior alkali halide phosphor. Also, the present phosphor may exert an improvement in response characteristics of stimulable emission and afterflow of stimulation, when irradiated with radiation and then stimulated and excited with either or both of visible ray and infrared ray, in comparison with the prior alkali halide phosphor.

Accordingly, the present stimulable phosphor is useful, in particular, as a phosphor for a radiation energy storage panel.

Moreover, the present stimulable phosphor may exert a high sensitivity to radiation and hence, if the present method for converting radiographic image is utilized for X-ray diagnosis and others, an X-ray exposed amount to the subject may be reduced. Further, the present stimulable phosphor has a high response speed to an exciting light and a high elimination speed of accumulated energy (i.e., afterglow), so that the present method for converting radiographic image may provide a

higher reading speed on radiation image and a more reduced time for eliminating after image, which leads to enhanced working efficiency of the system. Still further, a stimulable excited spectrum by the present stimulable phosphor may be extended to an oscillating wave region of a semi-conductor laser so that excitation with a semi-conductor laser may be feasible, whereby a reading apparatus for radiation image may be miniaturized and simplified with a more reduced cost. And, the present stimulable phosphor has a superior water vapor resistance and thus reduction in emission luminance by stimulation with lapse of time may be greatly improved.

CLAIMS

1. A radiation energy storage panel having a stimulable phosphor-containing layer characterized in that said stimulable phosphor is represented by the following formula:

$$(M_{1-x} \cdot M^{I}_{x})X \cdot aM^{II}X'_{2} \cdot bM^{III}X''_{3} \cdot cA{:}dB$$

wherein M represents either Cs or Rb; M^{I} represents at least one of alkaline metals selected from the group consisting of Li, Na, K, Rb and Cs; M^{II} represents at least one divalent metal selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni; M^{III} represents at least one metal selected from the group consisting of Se, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Cd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In; A represents at least one metal oxide selected from the group consisting of BeO, MgO, CaO, SrO, BaO, ZnO, Al_2O_3, Y_2O_3, La_2O_3, In_2O_3, SiO_2, TiO_2, GeO_2, SnO_2, Nb_2O_5, Ta_2O_5 and ThO_2; B represents at least one metal selected from the group consisting of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu, Mg, Pb, Bi, Mn and In; X, X' and X" each may by the same or different and represent a halogen atom selected from F, Cl, Br and I; x, a, b, c and d are numerals in the range of $0 \leq x \leq 1$, $0 \leq a \leq 1$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.5$ and $0 < d \leq 0.2$, respectively.

2. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 14, wherein said c is 0 and d is in the range of $0 < d \leq 0.2$.

3. A radiation energy storag panel having a stimulable phosphor-containing layer of Claim 15, wherein said x is 1.

4. A radiation en rgy storage panel having a stimulable phosphor-containing lay r of Claim 3, wherein said b is in the range of $0 \leq b \leq 1 \times 10^{-2}$.

5. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 4, wherein said M^{III} is selected from Y, La, Sm, Gd, Lu, Al, Ga and In.

6. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 5, wherein said X'' is selected from F, Cl and Br.

7. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 3, wherein said M^{II} is selected from Be, Mg, Ca, Sr and Ba.

8. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 3, wherein said M^{I} includes at least Rb or Cs.

9. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 8, wherein said A is selected from Tl, Nd, Ag and Cu.

10. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 4, wherein said d is in the range of $1 \times 10^{-6} \leq d \leq 0.1$.

11. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 2, wherein said x is in the range of $0 \leq x < 0.9$ and said A comprises Tl.

12. A radiation energy storage panel having a stimulable phosphor-containing layer of Claim 1, wherein said c is in the range of $0 < c \leq 0.2$ and said x is 1.

13. A method of converting a radiographic image which comprises the steps of:

(a) storing radiation energy-corresponding to a radiographic image in a stimulable phosphor of a panel comprising a stimulable phosphor-containing layer,

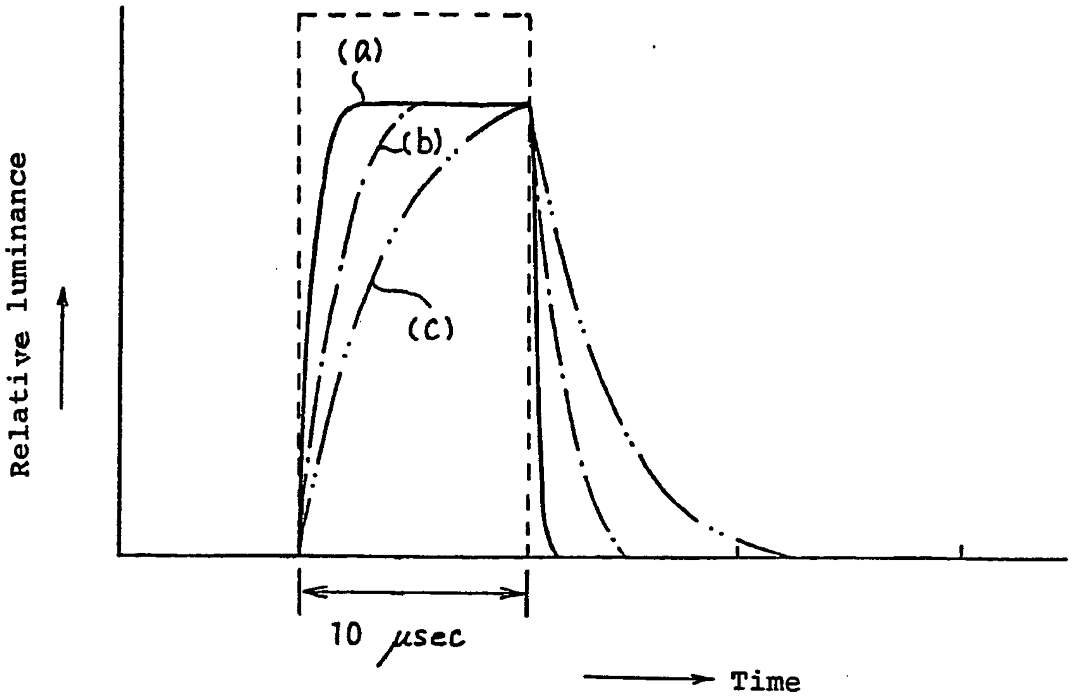
(b) scanning said layer with a stimulating ray to release said stored energy as a fluorescence, and

(c) detecting said fluorescence to form an image, wherein said stimulable phosphor is represented by the following formula:

$$(M_{1-x}\cdot M^{I}_{x})X\cdot aM^{II}X'_{2}\cdot bM^{III}X''_{3}\cdot cA{:}dB$$

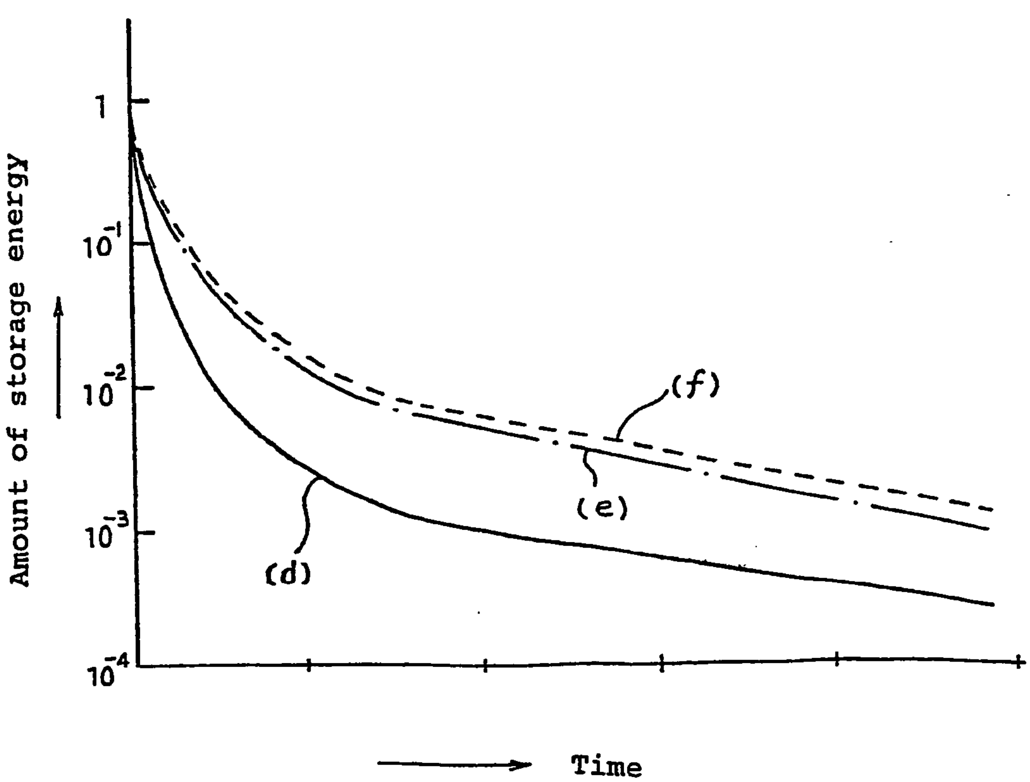
14. A method of converting a radiographic image of Claim 13 wherein said stimulating ray is a semoconductor laser.

Fig. 1



(a)
(b)
(c)
Relative luminance
10 μsec
Time

Fig. 2



1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
Amount of storage energy
(f)
(e)
(d)
Time

Fig. 3

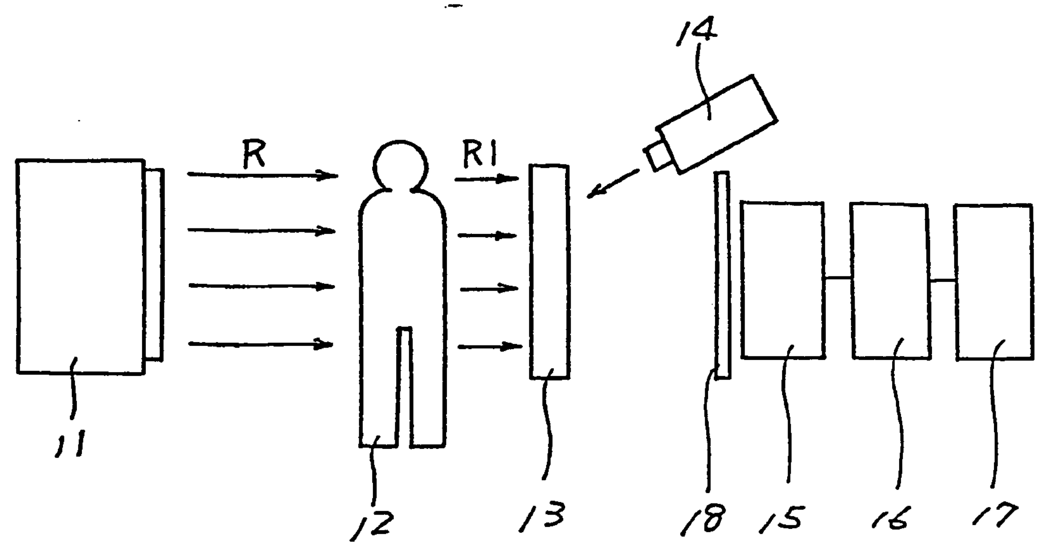

14
R
R1
11
12
13
18
15
16
17

Fig. 4

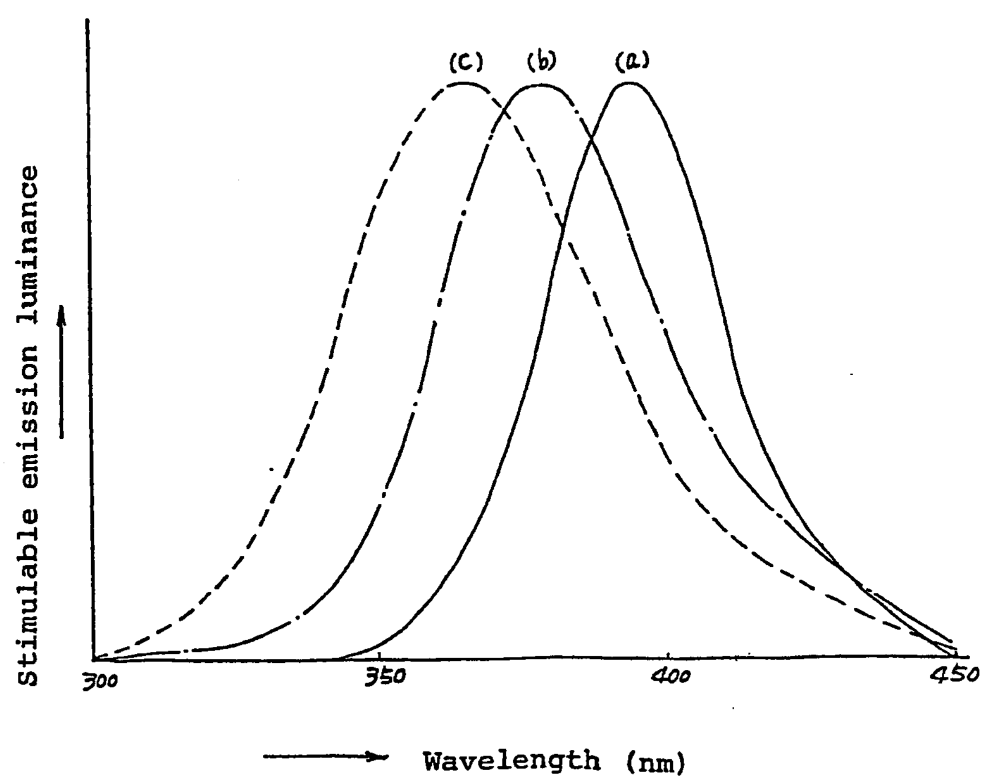

(c)
(b)
(a)
Stimulable emission luminance
300
350
400
450
Wavelength (nm)

Fig. 5

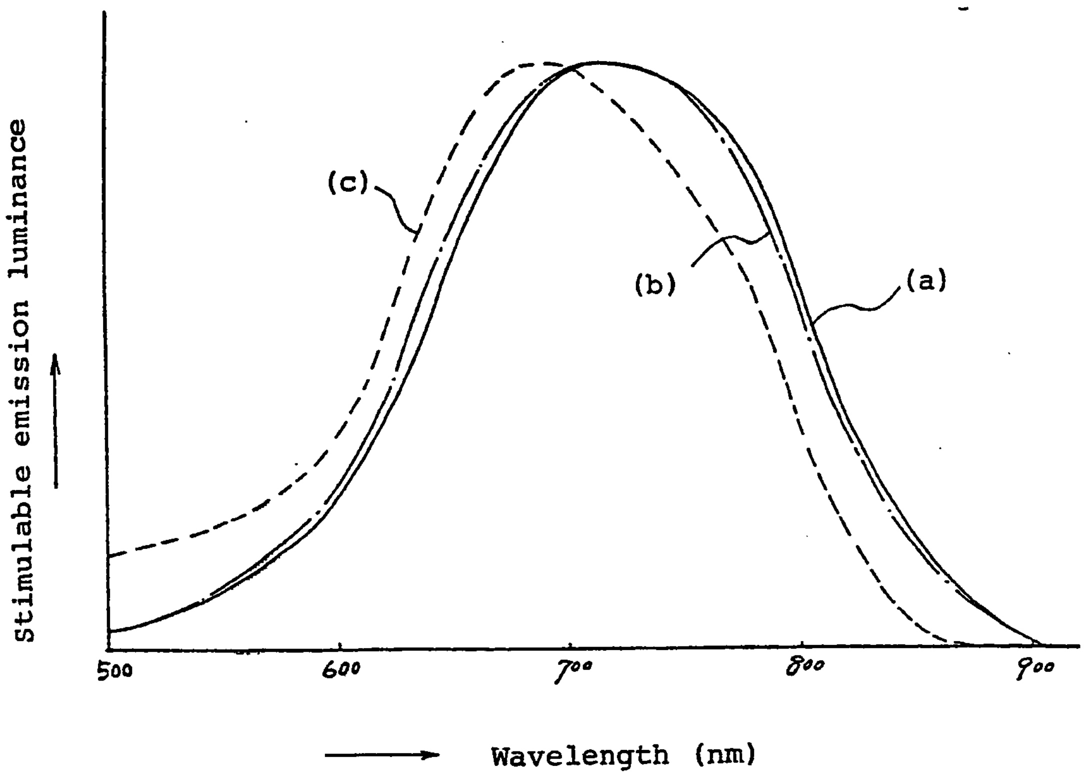

Stimulable emission luminance
(c)
(b)
(a)
500
600
700
800
900
Wavelength (nm)

Fig. 6

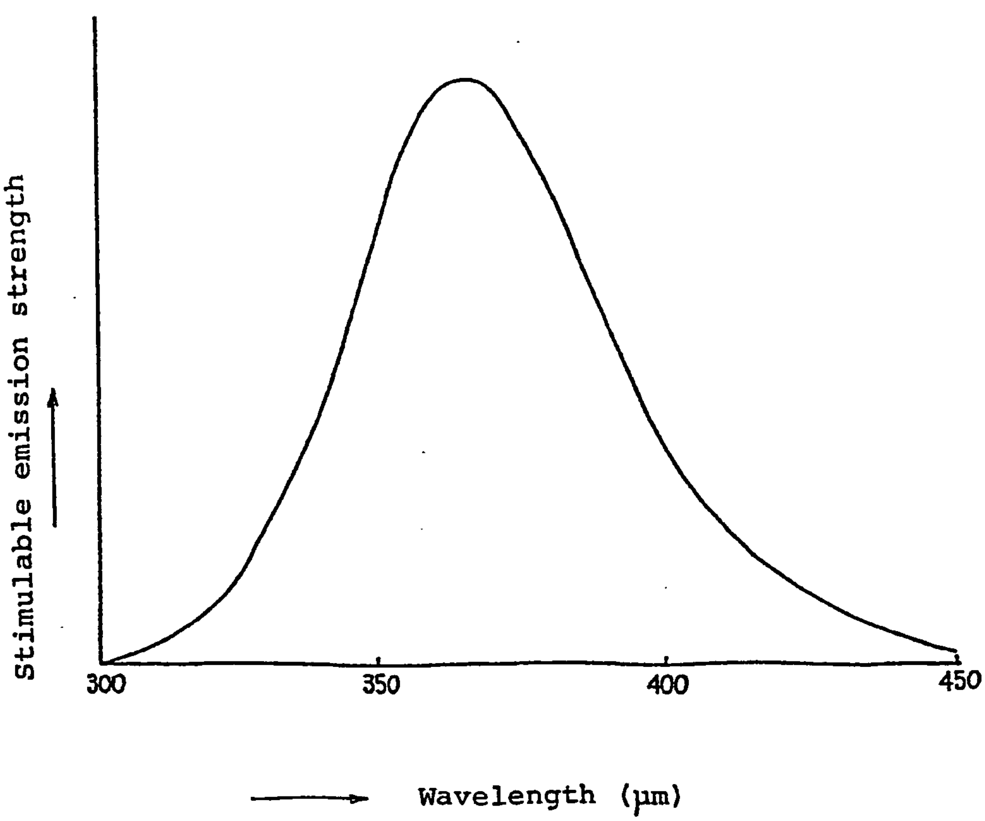

Stimulable emission strength
300
350
400
450
Wavelength (μm)

Fig. 7

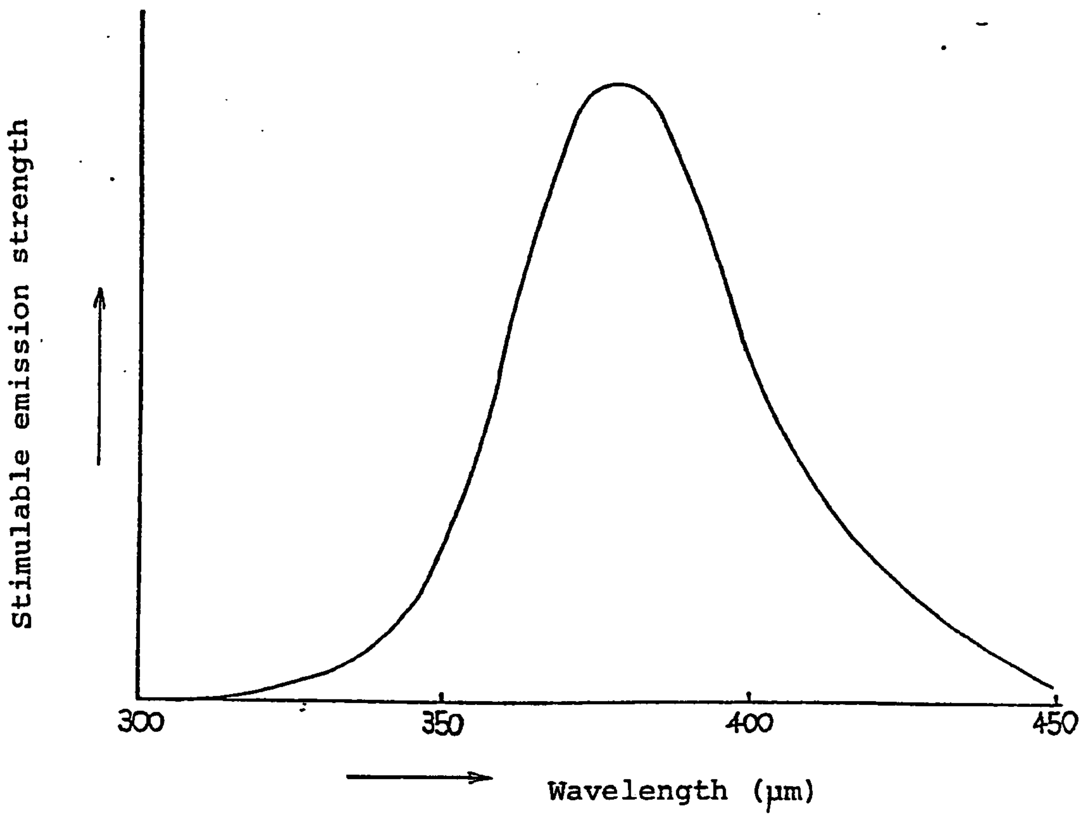

Stimulable emission strength
300
350
400
450
Wavelength (µm)

Fig. 8

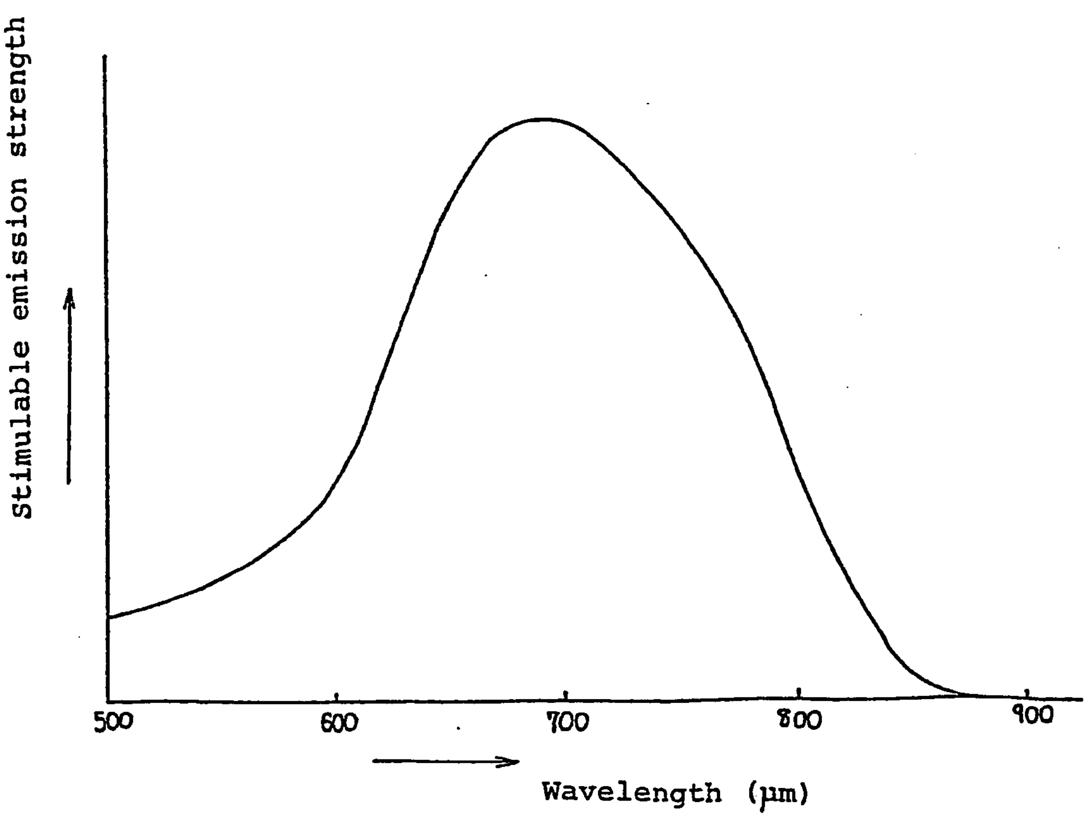

Stimulable emission strength
500
600
700
800
900
Wavelength (µm)

Fig. 9

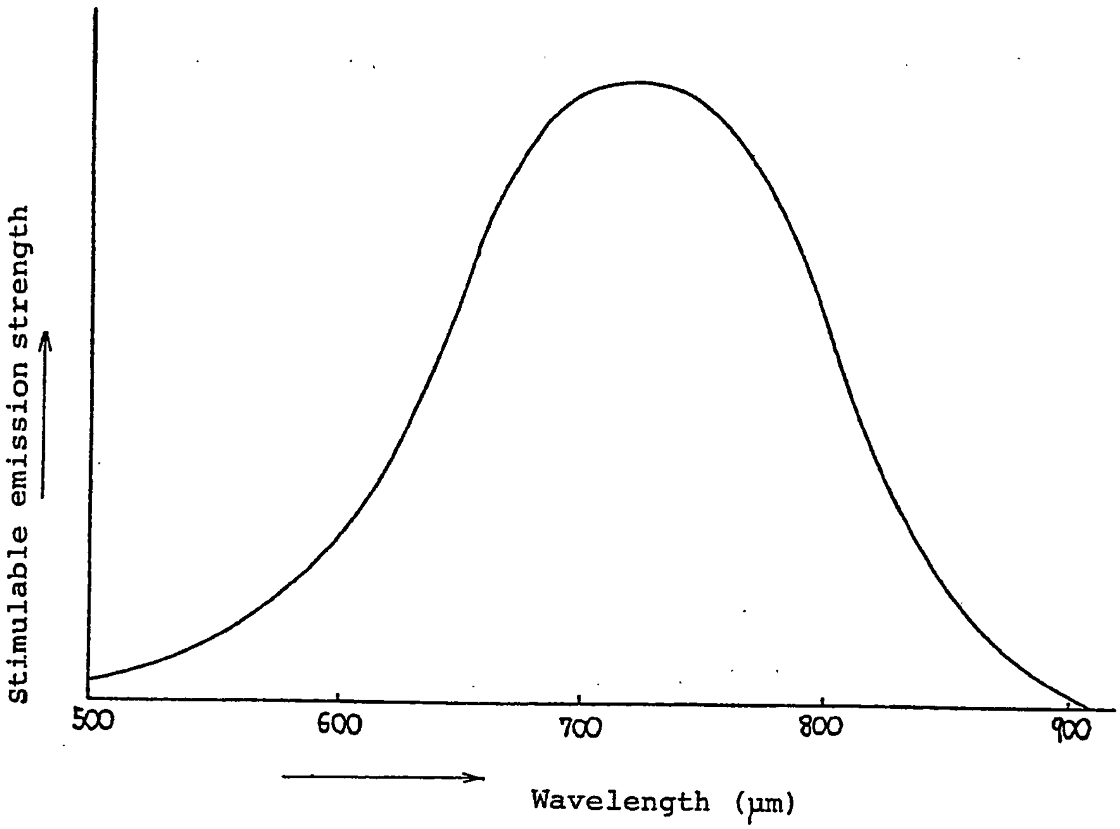
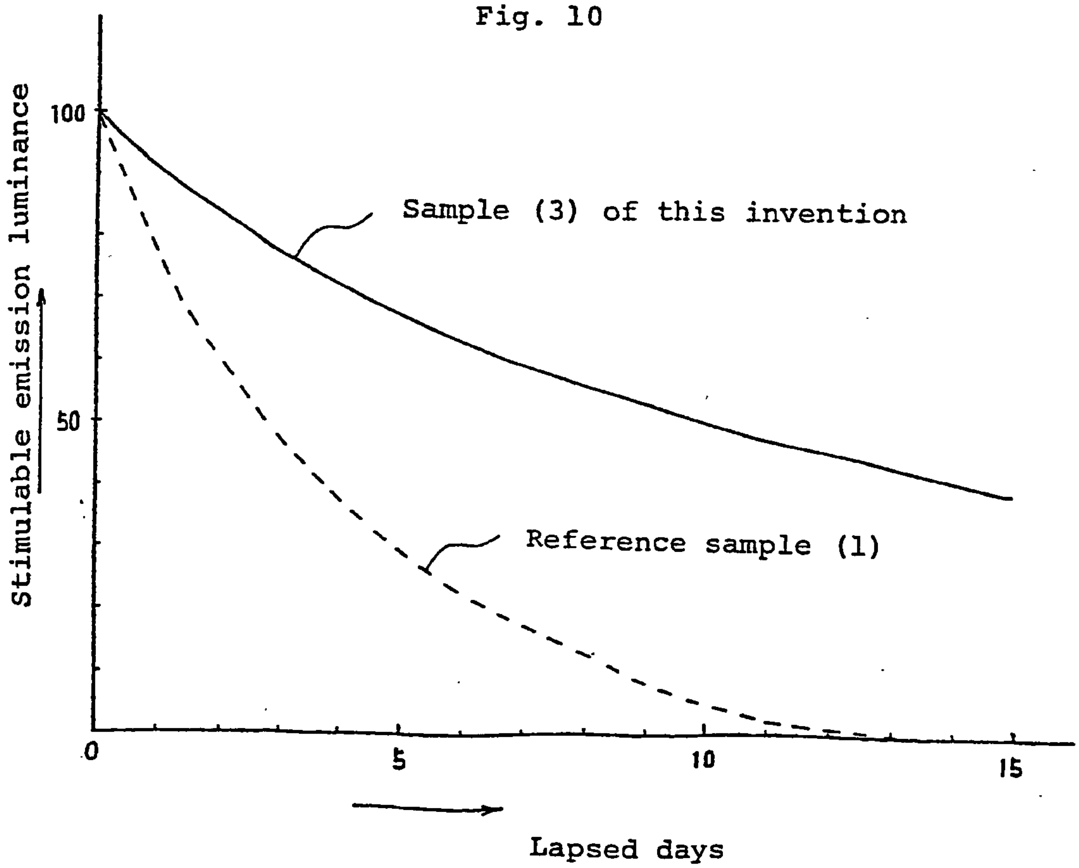

Stimulable emission strength
500
600
700
800
900
Wavelength (µm)

Fig. 10


Stimulable emission luminance
100
50
0
5
10
15
Sample (3) of this invention
Reference sample (1)
Lapsed days